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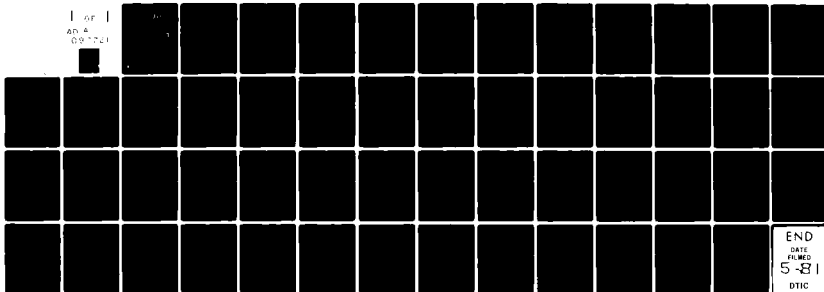
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ION-ION NEUTRALIZATION

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20. Abstract The results are described from two aspects of the programme. (i) A Coordinated Selected Ion Flow Tube (SIFT) and Flowing Afterglow/Langmuir Probe (FALP) study of switching and ion-ion neutralization reactions of several stratospheric ions. It is shown that CH_3CN is a viable candidate for molecule X in the recently observed stratospheric ions $\text{H}_2^+(\text{H}_2\text{O})_n \text{X}_m$ and that their neutralization rate coefficients are similar to those for mesospheric cluster ions. (ii) A study of the collision enhancement in helium of two ion-ion neutralization rate coefficients, (α_2) , in the pressure range 0.5 to 8 Torr. (α_2) is seen to increase more rapidly with pressure than expected from previous high pressure data. Estimates are made of the appropriate values for (α_2) in the stratosphere. alpha 2'		

PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies, conducted by the authors of this report, which includes determinations of ion-molecule reaction rate coefficients and product ion distributions, electron-ion recombination coefficients and electron attachment coefficients. The work is largely intended as a contribution to the physics and chemistry of natural plasmas such as the Earth's atmosphere and the interstellar medium. A great deal of relevant data has been obtained principally because of our successful development and exploitation of the Langmuir Probe/Flowing Afterglow (FALP) and Selected Ion Flow Tube (SIFT) techniques. Parts of the overall programme are supported by the Science Research Council.

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I INTRODUCTION

During the last few years, we have developed two major experiments designed to study ionic reactions at low temperatures which occur in natural plasmas such as the Earth's ionosphere and interstellar gas clouds. These experiments are (i) The Selected Ion Flow Tube (SIFT) which we have used to study a large number of ion-molecule reactions over a temperature range of 80 K - 550 K. (ii) The Flowing Afterglow/Langmuir Probe (FALP) which we have used to study several plasma interaction processes, the major effort being directed towards ion-ion neutralization reactions, the subject area for which we are currently funded by AFOSR and with which this report is concerned.

Our approach to the study of ion-ion mutual neutralization (ionic recombination) was first to measure the binary recombination coefficients, α_2 , of the 'simple' ions which are known to exist in the upper atmosphere (e.g. $\text{NO}^+ + \text{NO}_2^-$, $\text{O}_2^+ + \text{CO}_3^-$ etc.) and then to follow these studies by measuring α_2 for several reactions involving 'cluster' ions (e.g. $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{NO}_3^- \cdot \text{HNO}_3$ etc) which are known to be the dominant ion types in the lower mesosphere. We were also able to study the temperature dependence of α_2 for two reactions which indicated a dependence in accordance with theoretical predictions. As a result of this work we have been able to suggest the appropriate values of α_2 to be used in mesospheric de-ionization rate calculations. Details of the technique and the results of these studies have been given in previous reports and are reported in several scientific papers, the references to which are given in the scientific papers 1 and 2 which are included as the major part of this report.

The work with which this report is concerned represents an extension of the research programme outlined above and relates to two aspects of stratospheric ion chemistry.

(i) Switching Reactions and Mutual Neutralization Rates of Stratospheric Ions.

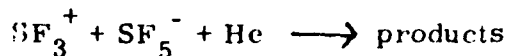
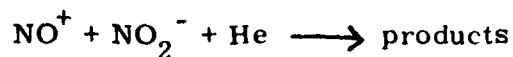
Details of this part of the programme are given in Paper 1 (Planetary and Space Science, In Press) together with all relevant references and so only a brief review will be given here.

During the last year balloon-borne mass spectrometers have been flown by other groups to determine the positive and negative ions present in the stratosphere. Not surprisingly, all are clustered species, the negative ions being of the kind $\text{NO}_3^- (\text{HNO}_3)_n$, $\text{HSO}_4^- (\text{HNO}_3)_n$, $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_n$ and $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_n (\text{HNO}_3)_m$ and the positive ions being of the type $\text{H}^+ (\text{H}_2\text{O})_n$ and $\text{H}^+ (\text{H}_2\text{O})_n \text{X}_m$ where $\text{X} = 41$ amu. A possible candidate for X is CH_3CN although this is by no means certain. Thus we have used our SIFT apparatus to study the reactions of CH_3CN with the well established stratospheric species $\text{H}^+ (\text{H}_2\text{O})_n$ in order to test the hypothesis that CH_3CN will replace H_2O in the $\text{H}^+ (\text{H}_2\text{O})_n$ ions and so generate the ion series $\text{H}^+ (\text{H}_2\text{O})_n (\text{CH}_3\text{CN})_m$. This does indeed occur (see below and Paper 1) and following this we then proceeded to use the FALP apparatus to determine α_2 for several reactions of the stratospheric positive and negative ions.

(ii) Laboratory Studies of Collision-Enhanced Ionic Recombination: Stratospheric Implications.

Details of this part of the programme are given in Paper 2 together with all relevant references. Paper 2 has been submitted for publication in Planetary and Space Science. Collision enhanced ionic recombination becomes increasingly important in ion-ion plasmas as the ambient gas pressure is increased and will eventually dominate the binary process referred to above. Studies of ternary ionic recombination have been carried out previously at pressures above about 30 Torr and up to pressures in excess of one atmosphere. No experiments have been carried out at the relatively low pressures appropriate to the middle stratosphere (1 - 10 Torr) which represents the transition region between low pressure pure binary ionic recombination (appropriate to the mesosphere) and high pressure ternary ionic recombination. With our existing FALP technique

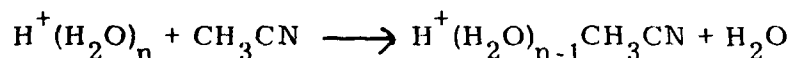
we are able to study ionic recombination up to a pressure of some 8 Torr in helium and so far we have exploited the technique to study the two reactions:



We have used the data obtained to estimate the rate coefficients for collision-enhanced ionic recombination, α_2^i , appropriate to the complex ions present in the stratospheric gas.

II RESULTS

(i) The SIFT studies show that CH_3CN rapidly reacts with water cluster ions via switching reactions of the kind:



and generates other ions of the type $\text{H}^+(\text{H}_2\text{O})_n(\text{CH}_3\text{CN})_m$ via further sequential switching reactions. An interesting and important observation from these studies is that total replacement of H_2O in the ubiquitous mass 73 amu atmospheric ion $\text{H}^+(\text{H}_2\text{O})_4$ does not take place, the ion $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ being a very stable, unreactive ion. We were therefore able to study the mutual neutralization of the stratospheric positive ions $\text{H}^+(\text{H}_2\text{O})_4$ and $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ with several stratospheric negative ions in the FALP apparatus. The detailed table of data is given in Paper 1.

(ii) The collision-enhanced ionic recombination coefficients, α_2^i , for both $\text{NO}^+/\text{NO}_2^-$ and $\text{SF}_3^+/\text{SF}_5^-$ increase approximately exponentially with pressure of the helium carrier gas, the latter reaction showing the greater increase (Fig. 2, Paper 2). We have suggested that this is due to the smaller mean free path of the heavier ions in the helium and on the basis of this premise we further suggest that α_2^i will increase rapidly in the atmospheric gas (N_2), in accordance with the higher pressure ternary ionic

recombination data of Mahan and Person (see references in Paper 2).

Thus, on the basis of these deductions, we have suggested the appropriate values of α_2^* to be used in stratospheric de-ionization rate calculations.

III CONCLUSIONS

The results obtained from part (i) of the programme are significant in two respects. Firstly, the SIFT data strongly suggests that CH_3CN is a viable candidate for species X in the stratospheric ion series $\text{H}^+(\text{H}_2\text{O})_n \cdot \text{X}_m$ and so it seems very probable that the major stratospheric positive ions are of the type $\text{H}^+(\text{H}_2\text{O})_n$ and $\text{H}^+(\text{H}_2\text{O})_n (\text{CH}_3\text{CN})_m$, although final confirmation of this is required (an important requirement is to identify an adequate source of CH_3CN in the stratosphere). Secondly, the measured binary recombination coefficients, α_2 , for several reactions involving stratospheric positive and negative ions, indicate that $\alpha_2 \approx (5-6) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ these values being insignificantly different from the α_2 values relating to mesospheric ions, a satisfying result from the standpoint of atmospheric de-ionization rate calculations. A profitable extension of the work would be to measure α_2 for more highly clustered ions at mesospheric and stratospheric temperatures.

The major conclusion to be drawn from part (ii) of the programme is that a faster-than-previously expected increase occurs in the collisional-enhanced ionic recombination coefficient, α_2^* , at altitudes below 45 kms in the stratosphere. At 40 kms, $\alpha_2^* \sim 2\alpha_2$. On the basis of previous high pressure data extrapolated to low pressures, we had previously estimated that α_2^* was approximately $2\alpha_2$ at a significantly lower altitude (~ 30 km). At about 35 km where several recent balloon-borne in situ experiments have been carried out, the effective binary ionic recombination rate coefficient is now estimated to be $\sim 2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, almost a factor of two larger than our previous estimates had indicated.

Clearly, further measurements of α_2' are required, including temperature dependence studies. Theory predicts that α_2 varies as $T^{-\frac{1}{2}}$ (our experiments confirm this for 2 reactions) and that the high pressure ternary recombination varies as $T^{-2.5}$ or T^{-3} . A study of the temperature dependence of α_2' in the intermediate pressure régime could be very instructive from both a stratospheric and a fundamental viewpoint. It is also important to study α_2' for reactions occurring in different buffer gases, nitrogen being of obvious interest since we have suggested that α_2' will increase rapidly with N_2 pressure. These studies will form a significant part of our research effort in the coming year when our new temperature variable FALP apparatus will be fully operational.

PAPER 1

ION-ION MUTUAL NEUTRALIZATION AND ION-NEUTRAL
SWITCHING REACTIONS OF SOME STRATOSPHERIC IONS

Planetary and Space Science (In Press)

ION-ION MUTUAL NEUTRALIZATION AND
ION-NEUTRAL SWITCHING REACTIONS OF
SOME STRATOSPHERIC IONS

by

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Short Title: Ion-Ion and Ion-Neutral Reactions in the Stratosphere

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Abstract

Following the recent mass spectrometric observations of the ambient stratospheric positive and negative ions, we have carried out co-ordinated laboratory experiments using a selected ion flow tube apparatus and a flowing afterglow apparatus for the following purposes.

- (i) To consider whether CH_3CN is a viable candidate molecule for the species X in the observed stratospheric ion series $\text{H}^+(\text{H}_2\text{O})_n(\text{X})_m$ and
- (ii) to determine the binary mutual neutralization rate coefficients, α_i , for the reactions of $\text{H}^+(\text{H}_2\text{O})_4$ and $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ with several of the negative ion species observed in the stratosphere. We conclude from (i) that CH_3CN is indeed a viable candidate for X and from (ii) that the α_i for stratospheric ions are within the limited range $(5-6) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$.

INTRODUCTION

The major positive ions present in the mesosphere are known to be the cluster ions $H_3O^+(H_2O)_n$ - hydrated hydronium ions (alternatively designated here $H^+(H_2O)_{n+1}$ - proton hydrates) as a result of the pioneering measurements of Narcisi and his colleagues (Narcisi and Bailey, 1965; Narcisi and Roth, 1970), substantiated by the work of Goldberg and Aikin (1972) and Arnold and Krankowsky (1977 a,b). The negative ions are predominantly the "simple" ions CO_3^- , HCO_3^- , NO_3^- and their hydrates, the $CO_3^-(H_2O)_n$, $NO_3^-(H_2O)_n$ and $NO_3^-(HNO_3)_n$ cluster ions (Krankowsky et al., 1972; Narcisi et al., 1974). In previous experiments in this laboratory the binary positive ion/negative ion mutual neutralization rate coefficients, α_i , (ionic recombination coefficients) for many reactions involving these mesospheric ions have been measured (Smith and Church, 1976; Smith et al., 1976; Smith et al., 1978b) and the most appropriate values of α_i for atmosphere de-ionization rate calculations have been suggested (Smith and Church, 1977).

The higher ambient pressures in the stratosphere present a more challenging problem in mass spectrometry and so data concerning the ionic content of this region have only recently been obtained and then only within the limited altitude range of approximately 30-40km using balloon-borne mass spectrometers. Thus the data of Arnold and Krankowsky and their colleagues (Arnold et al., 1977, 1978), of Olson et al. (1977) and of Arijs et al. (1978) indicate the presence of the inevitable proton hydrates $H^+(H_2O)_n$ coexisting with another group of ions $H^+(H_2O)_n X_m$. On the basis of the earlier (erroneous) indication of the mass of X (= 40 amu) together with thermodynamic reasoning, Ferguson (1978) suggested that X was probably NaOH. However, the

most recent measurements show that X has a mass of 41 amu (Arnold, 1980; Arijs et al., 1980/81). A possible designation for X is CH_3CN (methyl cyanide or acetonitrile), one of the possibilities suggested by Arnold et al. (1978) on the basis of their earliest measurements, although as yet no satisfactory mechanism for the production of CH_3CN in the stratosphere has been identified. Data have also been obtained relating to the negative ion content of the stratosphere and these indicate the dominance of large cluster species of the type $\text{NO}_3^-(\text{HNO}_3)_n$, $\text{HSO}_4^-(\text{HNO}_3)_n$, $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$ and $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n(\text{HNO}_3)_m$ (Arnold and Henschen, 1978; Arnold and Fabian, 1980; Arijs et al., 1981), designations supported by flowing afterglow experiments on the production and reactions of such ions, carried out in the NOAA laboratories in Boulder (Fehsenfeld et al., 1975; Viggiano et al., 1980).

Stimulated by the in-situ observations, we describe in this paper measurements of the binary mutual neutralization rate coefficients for several reactions involving some of these stratospheric positive and negative ions using our flowing afterglow/Langmuir probe apparatus. In associated studies using a selected ion flow tube (SIFT) apparatus we have demonstrated that CH_3CN can rapidly displace H_2O from $\text{H}^+(\text{H}_2\text{O})_n$ ions and thus CH_3CN is a credible candidate for X in the $\text{H}^+(\text{H}_2\text{O})_n \text{X}_m$ stratospheric ions. These data also provided crucial information which allowed us to satisfactorily pursue some of the ionic recombination measurements.

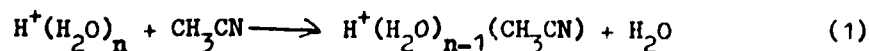
EXPERIMENTAL

Details of the flowing afterglow / Langmuir probe (FALP) and selected ion flow tube (SIFT) experiments have been given in previous publications and so only the essential features and those details specific to the present series of experiments will be referred to here.

The SIFT Experiment

This has been described in detail in a recent review (Smith and Adams, 1979). In essence, it involves the injection of a mass analysed beam of ions into a fast flowing carrier gas (helium in these experiments), in which the ions thermalize by collision as they are convected down a flow tube. Reactant gases are added to the carrier gas and the reaction rate coefficients and product ion distributions are determined by correlating the primary and product ion signals, observed by a downstream mass spectrometer detector, with the rate of addition of the reactant gas.

In the present experiments, $H^+(H_2O)_n$ ions ($n = 1$ to 4) were generated in a subsidiary flow tube ion source (the details have been recently discussed by Smith and Adams, 1980) and injected into the flowing carrier gas with low energies (< 10 eV in the laboratory frame) in order to inhibit their fragmentation in collision with the helium atoms. Controlled amounts of CH_3CN were introduced into the main flow tube by monitoring the flow rate of a prepared helium/ CH_3CN mixture of known partial pressures of the two components (30 torr of CH_3CN in 1000 torr of helium). Thus reactions of the kind:



were observed to occur and their rate coefficients were determined in the usual way. Sequential reactions with CH_3CN were also studied. The measurements were made at temperatures of 200 and 300 K. The total absence of water vapour from the main flow tube allowed the study of reaction (1) without complications due to its reverse reaction which regenerates the proton hydrates. Such is an important consideration in the stratosphere (see below).

The FALP Experiment

Detailed discussions of the technique have been given in previous publications (Smith and Church, 1976; Smith et al., 1978b). The major requirement is to generate a positive ion/negative ion flowing afterglow plasma totally devoid of electrons and in which ideally either only one positive ion species and/or only one negative ion species exists. Under these conditions, a movable Langmuir probe is able to determine the ion density in the flowing afterglow plasma at any point on the axis of the plasma column. Thus ionic recombination coefficients can be determined by measuring the ion density gradient along the plasma column and hence the time rate of change of ion density with a knowledge of the plasma flow velocity (Adams et al., 1975). The positive and negative ions in the plasma were identified using a downstream quadrupole mass spectrometer.

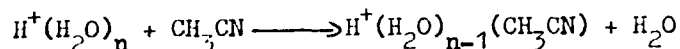
In these experiments it is a simple matter to establish $\text{H}^+(\text{H}_2\text{O})_4$ as the dominant ion in the afterglow by introducing controlled amounts of water vapour upstream or downstream of the microwave discharge which generates the afterglow plasma (see Smith et al., 1978b for further details). From the SIFT studies described in the next section, we discovered that by the addition of sufficient CH_3CN into the $\text{He}/\text{H}_2\text{O}$ afterglow the $\text{H}^+(\text{H}_2\text{O})_4$ ions were converted exclusively to the

$\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ ions, an observed stratospheric ion species (assuming $\text{X} = \text{CH}_3\text{CN}$). Both the H_2O and CH_3CN were introduced into the flow tube by bubbling helium through the respective liquids and hence passing the saturated helium/vapour mixture into the flow tube. The negative ion species were generated by passing electron attaching gases at appropriate flow rates through the microwave discharge. Thus, by using NO_2 , the ions NO_3^- , $\text{NO}_3^-(\text{HNO}_3)_{1,2}$ could be generated in varying fractions and by using $\text{SO}_2/\text{H}_2\text{O}$ mixtures, HSO_4^- , $\text{HSO}_3^-(\text{H}_2\text{O})$ and $\text{HSO}_2^-(\text{H}_2\text{O})$ could be generated in varying fractions. To generate the sulphur containing negative ions it was also necessary to introduce the H_2O upstream of the discharge. Cl^- ions are readily generated as the only negative ion species in the afterglow by adding Cl_2 upstream of the microwave discharge. Ionic recombination coefficients were determined for various combinations of the types of positive and negative ion species. All measurements were made at a temperature of about 300 K.

RESULTS

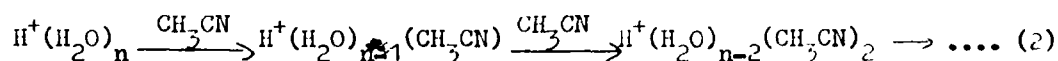
SIFT Data

Rate coefficients, k , were measured at 200 K and 300 K for the switching reactions:

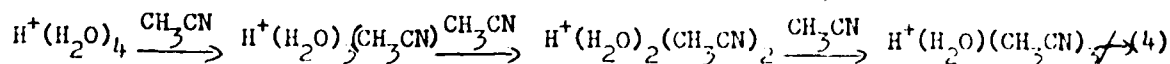
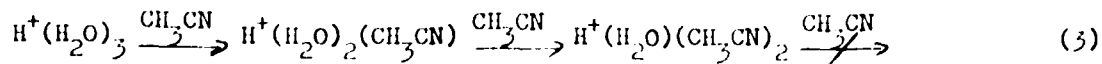


for $n = 1$ to 4. The results obtained are presented in Table 1 together with the gas kinetic rate coefficients, k_{ADO} , calculated using the ADO theory of Su and Bowers (1975). The reactions proceed very rapidly, essentially at the gas kinetic limiting rate within the accuracy of the experimental data ($\pm 30\%$ on the measured rate coefficients). The significantly smaller k for the larger proton hydrates is in accordance with the larger reduced mass of the reactants, whilst the very large absolute values of k and k_{ADO} are a consequence of the large polarizability (Le Fevre, 1965) and dipole moment (Nelson et al., 1967) of CH_3CN .

Sequential switching reactions of the kind

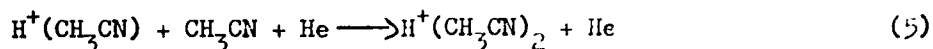


were observed to proceed rapidly. Thus $\text{H}^+(\text{H}_2\text{O})_2$ was readily converted to $\text{H}^+(\text{CH}_3\text{CN})_2$. However for the higher order hydrates $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$, complete replacement of the H_2O was not observed and at both temperatures the reaction sequences terminated with the ion retaining one H_2O molecule:



Thus the terminating ions in these series were $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_2$ and $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$. The ions $\text{H}^+(\text{CH}_3\text{CN})_3$ and $\text{H}^+(\text{CH}_3\text{CN})_4$ were not produced

at significant rates. It is however worthy of note that during the course of our measurements we observed that the three-body association reaction:

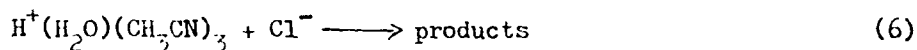


proceeded extremely rapidly at 200 K, the estimated rate coefficient being about $1 \times 10^{-25} \text{ cm}^6 \text{ s}^{-1}$. Further addition of CH_3CN proceeded only very slowly. These observations are in accord with the thermodynamic data of Meot-Ner (1978) which show that the bonding of the third CH_3CN in the $\text{H}^+(\text{CH}_3\text{CN})_3$ ion is relatively weak. Our kinetic data indicate that the $\text{H}^+(\text{CH}_3\text{CN})_2 - \text{H}_2\text{O}$ bonding is significantly stronger than the $\text{H}^+(\text{CH}_3\text{CN})_2 - \text{CH}_3\text{CN}$ bonding and similarly the $\text{H}^+(\text{CH}_3\text{CN})_3 - \text{H}_2\text{O}$ bonding is stronger than that of $\text{H}^+(\text{CH}_3\text{CN})_3 - \text{CH}_3\text{CN}$. However structural differences in these ions may critically influence their relative stabilities.

FALP Data

Data were obtained for the mutual neutralization of two stratospherically observed positive ions, $\text{H}^+(\text{H}_2\text{O})_n$ and $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ (assuming $X = \text{CH}_3\text{CN}$) with several observed stratospheric negative ions. The summarised binary recombination coefficient data (α_i) are given in Table 2. The α_i were obtained from linear plots of the reciprocal positive ion density as a function of distance (and hence recombination time) along the after-glow plasma column. Both the positive and negative ions present in the downstream part of the plasma were identified by the quadrupole mass spectrometer located there. Unfortunately we were not able to generate plasmas in which only a single stratospheric negative ion species existed with the above positive ion species (see Table 2). However since a single positive ion species was present, then the ion density in the plasma and

the mean mass of the negative ion species could be obtained readily using the Langmuir probe. That the latter correlated with the mean negative ion mass as determined by the downstream mass spectrometer indicates that the fractions of the various negative ions remained essentially invariant along the length of the plasma column. The data in Table 2 show that α_i for all of the reactions lie within the limited range $(5-6) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. Such is also the case for the relatively simple reaction:



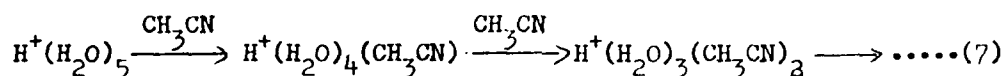
involving the simple negative ion species Cl^- which we have previously shown also reacts at a very similar rate with $\text{H}^+(\text{H}_2\text{O})_4$ (Smith et al., 1978b). The relative invariance of α_i with the nature and complexity of the reacting positive and negative molecular ions (clustered or not) is consistent with all our previous data for these binary neutralization reactions. We have suggested reasons for this phenomenon in previous publications (Smith and Church, 1977; Smith et al., 1978b); it is sufficient to restate here that these neutralization processes are extremely rapid and efficient occurring with large mean thermal cross-sections $\gtrsim 10^{-12} \text{ cm}^2$. It is worthy of note that when both the positive and negative ions are atomic then the α_i are smaller by at least 2 orders of magnitude (Church and Smith, 1978).

STRATOSPHERIC IMPLICATIONS

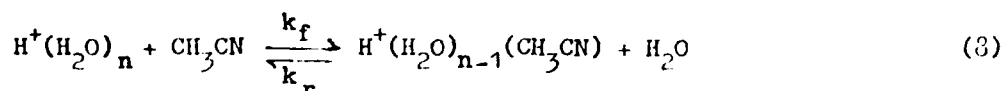
The SIFT experiments show that CH_3CN rapidly replaces H_2O in proton hydrates and therefore the presence of CH_3CN in the stratosphere would result in the formation of the $\text{H}^+(\text{H}_2\text{O})_m(\text{CH}_3\text{CN})_n$ ions via the reaction sequences indicated by equations (3) and (4). Very significantly, ions with masses equivalent to the ions included in these sequences have been observed in the stratosphere (Arnold et al., 1978; Arijs et al.,

1980/81) excluding those equivalent to $H^+(CH_3CN)_3$ and $H^+(CH_3CN)_4$ which also are not observed in our laboratory experiments. Whilst these observations do not constitute proof that $X = CH_3CN$, they clearly indicate that CH_3CN is a viable and likely candidate for X. Also no CH_3CN containing ions which originate from the lower order proton hydrates ($H^+(H_2O)_n$, $n = 1,2$) are observed in significant concentrations in the stratosphere consistent with the absence of these proton hydrate precursor ions from this region.

In the stratosphere, the higher-order proton hydrate $H^+(H_2O)_5$ is observed, together with the substituted ions which are presumably produced thus:

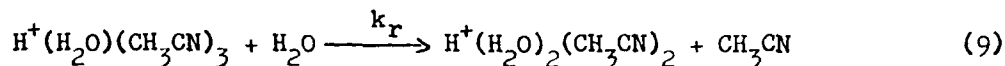


Unfortunately, by operating the ion source at room temperature, we were not able to generate sufficient densities of $H^+(H_2O)_5$ in our flow tube ion source (this must await the completion of a low temperature version) and so were not able to determine the terminating ion in this sequence (?). If H_2O and CH_3CN ($= X$?) co-exist in the stratosphere then the following equilibrium reactions need to be considered:



The very large rate coefficient for the forward reaction, k_f , relative to k_r ensures that only a small fraction of CH_3CN relative to H_2O would be necessary to allow a significant concentration of the mixed cluster ions to exist in the stratosphere. The fraction of CH_3CN/H_2O required to generate the observed equilibrium concentrations of the various ionic species is, of course, dependent on the equilibrium constants for the various reactions. Since we have shown that the k_f 's are gas kinetic and essentially temperature independent then we only require the

appropriate k_r 's at stratospheric temperatures. To date we have been able to obtain experimentally an upper limit to the rate coefficient for the endoergic reaction:



This is $\lesssim 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 300K and will presumably be lower at the lower temperatures of the stratosphere. Thus, if we can assume that a typical $k_r \lesssim 10^{-4} k_f$ then, for concentrations of $H^+(H_2O)_n X_m$ of about 10% of the concentrations of the $H^+(H_2O)_n$ ions, the CH_3CN concentration would only need to be $\leq 10^{-5}$ of the H_2O concentration. This is equivalent to a stratospheric mixing ratio for CH_3CN of $\sim 10^{-11}$ assuming a mixing ratio for H_2O of $\sim 10^{-6}$. At ~ 35 Km altitude where most of the in-situ data have been obtained, then the required concentration of CH_3CN ($= X$) is $\lesssim 10^7$ molecules cm^{-3} . Whilst this is a relatively small concentration, no adequate sources of CH_3CN in the stratosphere have yet been identified. However our previous SIFT studies of ion-molecule reactions of stratospheric interest (Smith et al., 1978a) have indicated that possible sources of C-N bonded compounds are the reactions of the N^+ and N_3^+ ion with hydrocarbons (e.g. CH_4) although such sources have to be justified quantitatively. More likely sources of cyanides are neutral-neutral reactions between nitrogen atoms and carbon bearing molecules.

The present recombination coefficient data (Table 2) together with the substantial amount of previous data for other reactant molecular ions indicate clearly that the α_i are relatively independent of the nature of the cluster ions and are therefore probably insensitive to the nature of X . Thus the α_i for the binary mutual neutralization of stratosphere-type positive and negative ions measured at a temperature of 300 K regardless of the actual nature of X will be within the very limited range of $(5-6) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. Assuming a temperature dependence

of $\alpha_i \sim T^{-1/2}$ which we have shown is valid for simpler positive ions over an appropriate temperature range and which is theoretically predicted for such reactions (Olson, 1972), then at the lowest stratospheric temperatures α_i would only increase by about 15% from the 300 K values. Thus an appropriate mean value for α_i to be used in stratospheric de-ionization rate coefficients is $(6 \pm 2) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, the uncertainty including the spread due to the temperature variations within the stratosphere and errors in the measurement of α_i .

No data are available concerning the nature of the neutral products of the mutual neutralization of cluster ions but it is to be expected for small cluster ions that the cluster molecules will be returned to the gas phase where they can undergo further reaction. However it is known that the recombination energy of the positive cluster ions, E_R , decreases and the electron detachment energy of the negative cluster ions, E_D , increases with increasing order of clustering. For even larger cluster ions, E_D can be larger than E_R and so for the interaction of two such ions, simple electron transfer cannot occur and so a "coalesced zwitterion" (Castleman, 1979) might form. These strongly polarized "neutral clusters" could then act as very efficient nucleation sites and initiate the rapid growth of aerosols in the stratosphere (see the discussion by Arnold, 1980b). In ion-ion mutual neutralization reactions for which $E_R \geq E_D$, their neutralization could occur producing fragment neutral clusters bound only by weak polarization forces (e.g. $(\text{H}_2\text{O})_n(\text{CH}_3\text{CN})_m$) and whilst such species would exist in low relative concentration and have a short lifetime in the stratosphere, they could nevertheless play a role in the stratosphere ion chemistry.

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REFERENCES:

- Adams, N.G., Church, M.J. and Smith, D. (1975).
J. Phys. D. 8, 1409
- Arijs, E., Ingels, J. and Nevejans, D. (1978).
Nature 271, 642
- Arijs, E., Nevejans, D., Frederick, P. and Ingels, J. (1981).
Geophys. Res. Letts. (submitted)
- Arijs, E., Nevejans, D. and Ingels, J. (1980/81).
Nature (in press)
- Arnold, F. (1980a).
(Private Communication)
- Arnold, F. (1980b).
Nature 284, 610
- Arnold, F., Böhrringer, H. and Henschen, G. (1978).
Geophys. Res. Letts. 5, 653
- Arnold, F. and Fabian, R. (1980).
Nature 283, 55
- Arnold, F. and Henschen, G. (1978).
Nature 257, 521
- Arnold, F. and Krankowsky, D. (1977a).
In: Dynamical and chemical coupling. (Ed. B. Grandal and J.A. Holtet) pp. 93. Reidel, Dordrecht, Holland.
- Arnold, F. and Krankowsky, D. (1977b).
J. Atmos. Terres. Phys. 39, 625
- Arnold, F., Krankowsky, D. and Marien, K.H. (1977).
Nature 267, 30
- Castleman, A.W., Jr. (1979).
Nucleation and Molecular Clustering about Ions. In: Advances in Colloid and Interface Science 10, 73-128. Elsevier, Amsterdam

Church, M.J. and Smith, D. (1978).

J. Phys. D. 11, 2199

Fehsenfeld, F.C., Howard, C.J. and Schmeltekopf, A.L. (1975).

J. Chem. Phys. 63, 2835

Ferguson, E.E. (1978).

Geophys. Res. Letts. 5, 1035

Goldberg, R.A. and Aikin, A.C. (1972).

EOS Trans. AGU 53, 1077

Krankowsky, D., Arnold, F. and Wieder, H. (1977).

In: Magnetosphere - ionosphere interactions. (Ed. K. Folkstad)

pp. 19-28. Oslo: Oslo University Press

Le Fevre, R.J.W. (1965).

Advan. Phys. Org. Chem. 3, 1

Mackay, G.I., Betowski, L.D., Payzant, J.D., Schiff, H.I. and Bohme, D.K. (1976).

J. Chem. Phys. 80, 2919

Meot-Ner, H. (1978).

J. Am. Chem. Soc. 100, 4694

Narcisi, R.S. (1974).

Ion and neutral composition measurements in the lower ionosphere.

In: Methods of measurement and results of lower ionospheric structure. (Ed. K. Rawer) pp. 207-218. Berlin: Akademie-Verlag

Narcisi, R.S. and Bailey, A.D. (1965).

J. Geophys. Res. 70, 3687

Narcisi, R.S. and Roth, W. (1970).

Adv. Electron. Electron Phys. 29, 79

Nelson, R.D., Lide, D.R., and Maryott, A.A. (1967).

NERDS-NBS No. 10

Olson, J.B., Amme, R.C., Brooks, J.N., Murcray, D.G. and Keller, G.E. (1977).

EOS Trans. AGU 58, 1201

Olson, R.E. (1972).

J.Chem. Phys. 56, 2979

Smith, D. and Adams, N.G. (1979).

In: Gas Phase Ion Chemistry (Ed. M.T. Bowers) Vol. 1, pp.1,
Academic Press, New York

Smith, D. and Adams, N.G. (1980).

J. Phys. D. 13, 1267

Smith, D., Adams, N.G. and Church, M.J. (1976).

Planet. Space Sci. 24, 697

Smith, D., Adams, N.G. and Miller, T.M. (1978a).

J. Chem. Phys. 69, 308

Smith, D., and Church, M.J. (1976).

Int. J. Mass Spectrom. Ion Phys. 19, 189

Smith, D., and Church, M.J. (1977).

Planet. Space Sci. 25, 433

Smith, D., Church, M.J. and Miller, T.M. (1978b).

J. Chem. Phys. 68, 1224

Su, T. and Bowers, M.T. (1975).

Int. J. Mass Spectrom. Ion Phys. 17, 211

Viggiano, A.A., Perry, R.A., Albritton, D.L., Ferguson, E.E. and
Fehsenfeld, F.C. (1980).

J. Geophys. Res. 85, 4551

Table 1

Rate coefficients and product ions for the reactions of $H^+(H_2O)_n$,
 $n = 1$ to 4, with CH_3CN at 200 K and 300 K.

Reactant Ion	Product Ion	Rate Coefficients, k , $\times 10^9$ ($cm^3 s^{-1}$)		
		Measured ^a		Calculated ^c k_{ADO}
		at 200 K	at 300 K	
$H^+(H_2O)$	$H^+(CH_3CN)$	4.5	4.6 ^b	3.93
$H^+(H_2O)_2$	$H^+(H_2O)(CH_3CN)$	4.0	4.0	3.21
$H^+(H_2O)_3$	$H^+(H_2O)_2(CH_3CN)$	3.5	3.7	2.92
$H^+(H_2O)_4$	$H^+(H_2O)_3(CH_3CN)$	3.2	3.5	2.76

- The rate coefficients are accurate to within $\pm 30\%$.
- Mackay et al. (1976) obtain $k = 4.7 \times 10^{-9} cm^3 s^{-1}$ for this reaction at 300 K.
- The values were calculated for a temperature of 300 K. The values for 200 K are insignificantly different (about 1% larger).

Table 2

Binary recombination coefficients for the mutual neutralization of $\text{H}^+(\text{H}_2\text{O})_4$ and $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ with mixtures of negative ion species at 300 K.

Positive Ion ^a	Negative Ions (%)	Recombination Coefficient $\times 10^8 \text{ (cm}^3\text{s}^{-1}\text{)}$
$\text{H}^+(\text{H}_2\text{O})_4$	HSO_4^- 30 $\text{NO}_3^-(\text{H}_2\text{O})$ 30 $\text{NO}_3^-(\text{HNO}_3)$ 15 140 amu 25	5.9
$\text{H}^+(\text{H}_2\text{O})_4$	HSO_4^- 35 $\text{HSO}_3^-(\text{H}_2\text{O})$ 25 $\text{HSO}_2^-(\text{H}_2\text{O})$ 20 SO_3^- 20	6.6
$\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$	Cl^- 95	6.8
$\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$	NO_3^- 65 NO_2^- 35	6.3
$\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$	$\text{NO}_3^-(\text{HNO}_3)$ 60 NO_3^- 40	5.9
$\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$	$\text{NO}_3^-(\text{HNO}_3)$ 40 HSO_4^- 30 140 amu 30	5.9
$\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$	HSO_4^- 30 SO_3^- 30 $\text{HSO}_2^-(\text{H}_2\text{O})$ 25 $\text{HSO}_3^-(\text{H}_2\text{O})$ 15	5.8

a. In each case $\text{H}^+(\text{H}_2\text{O})_4$ or $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$ was greater than 99% of the positive ion content of the plasma.

PAPER 2

LABORATORY STUDIES OF COLLISION-ENHANCED
IONIC RECOMBINATION: STRATOSPHERIC IMPLICATIONS

Planetary and Space Science (Submitted)

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LABORATORY STUDIES OF COLLISION -
ENHANCED IONIC RECOMBINATION:
STRATOSPHERIC IMPLICATIONS.

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Short Title: Collision - Enhanced Ionic Recombination.

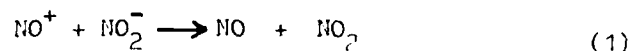
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ABSTRACT:

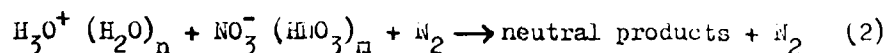
Measurements are described of the dependence on helium pressure (0.5 to 8 Torr) of the neutralization coefficients, α'_2 , for the reactions (i) $\text{NO}^+ + \text{NO}_2^- + \text{He}$ and (ii) $\text{SF}_3^+ + \text{SF}_5^- + \text{He}$. α'_2 is observed to increase approximately exponentially with pressure from the zero pressure pure binary coefficient, α_2 , the rate of increase of α'_2 being greater for (ii) than for (i). A qualitative explanation is suggested in terms of a mechanism involving the differing ion mean free paths in helium. These ideas are used, in combination with the higher pressure data of Mahan and Person, to obtain estimates for α'_2 for neutralization reactions of heavy ions in nitrogen. Thus approximate values for α'_2 for use in stratospheric de-ionization rate calculations are presented.

INTRODUCTION

The presence of electrons and negative ions in the mesospheric plasma ensures that charged particle neutralization occurs via electron-positive ion dissociative recombination and negative ion - positive ion mutual neutralization. The latter is often termed binary ionic recombination and is exemplified by the reaction



which, at the low ambient pressures of the mesosphere, is the only viable ionic recombination process. Below about 60km altitude in the stratosphere and troposphere, electrons are essentially absent and so (ignoring aerosol accretion) ionic recombination is the only neutralization process. In the higher pressure lower altitude regions, in addition to (1), the ternary ionic recombination process exemplified by:



must be considered. In (2) the neutralization rate is enhanced by the presence of the (third body) M_2 molecule, the efficiency of such reactions increasing with the concentration of the third body. This and other aspects of atmosphere ion chemistry have recently been reviewed by Smith and Adams (1986).

The most detailed study of binary ionic recombination has been carried out by Smith and his colleagues using a flowing afterglow/Langmuir probe (FALP) technique (Smith and Church, 1976; Smith et al., 1976, 1978). The measurements were carried out at 300K in a helium carrier gas at pressures up to about one Torr for a variety of mass identified small and clustered, positive and negative ions. The binary recombination coefficient, α_2 , was independent of the helium pressure indicating that no significant contribution to the neutralization was occurring via ternary processes (i.e. (2)). Additionally, two other recombination

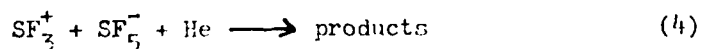
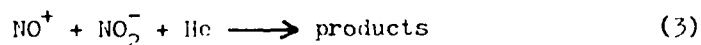
studied over a limited temperature range (Smith and Church, 1977), and α_2 was observed to vary as T^{-1} in accordance with the theoretical prediction of the absorbing sphere model of Olson (1972). An important, feature of the results of these studies is the relatively small differences in α_2 for reactions involving positive and negative ions of widely varying complexities. On the basis of their data and of previous data on the ternary process from other workers, Smith and Church (1977) have indicated the appropriate values of α_2 to be used in atmospheric de-ionization rate calculations and also indicated that below about 30km in the atmosphere, ternary ionic recombination increasingly dominates over the binary process.

The ternary process was studied extensively during the first half of this century, both experimentally and theoretically. Most effort was directed towards the so-called Thomson régime (the intermediate pressure range, $\sim 100 - 1000$ Torr) and to the so-called Langevin - Harper régime (the high pressures régime, above about 1000 Torr). More recent experimental work has extended the investigations to pressures as low as a few tens of Torr (Mahan and Ierson, 1964; McGowan, 1967). The results of these studies have been discussed in several reviews (e.g. Sayers, 1962; Flannery, 1972, 1976; Mahan, 1974). The most recent experiments have been carried out by Sennhauser and Armstrong (1978, a,b,) who have determined ternary coefficients in $\text{NH}_3/\text{N}_2\text{O}$ mixtures within the pressure range 35 - 1200 Torr at 298K and compared their results with their own theoretical model. All this previous data was obtained without mass identification of the ions involved in the neutralization process, the ion identifications being guessed at from ion-chemical reasoning. The recent theoretical work is mostly due to Bates and his colleagues (Bates and Moffett 1966, Bates and Flannery 1968, Bates and Mendes 1975, 1978 a, b) which relates to the low and intermediate pressure régimes. The most recent review of the subject

is that given by Bates (1979).

There is now a need to study the very low pressure régime (clarified later) in which the pure binary mutual neutralization rate is just beginning to be enhanced by the onset of collisional effects. Such a situation obtains in the middle stratosphere, a region currently being investigated using balloon-borne instruments and in which data on ionic recombination rates (both binary and ternary) are important for de-ionization rate calculations (Arnold et al., 1977, 1978; Arnold 1980). Previously, estimates of effective recombination rates in this very low pressure régime have been obtained by extrapolating high pressure data ("An entirely unacceptable procedure" - Bates and Mendas (1978b), as we shall also see from the present data given in the Results section).

To provide some experimental data in this very low pressure régime, we have used our FALP technique to study at 500K the dependence on helium pressure of the effective binary recombination coefficients for two pairs of simple reactant ions:



These reactions were chosen for this initial study since the ions could be generated in sufficient concentrations and in the absence of significant clustering of the ions to other molecules at 300K even at the highest helium pressures ($\lesssim 10$ torr) at which we are able to use the FALP combination. Ideally, from an atmospheric viewpoint, nitrogen rather than helium would have been a more appropriate third body (carrier gas), but, in attempting to use this, experimental difficulties were encountered as referred to below. Nevertheless, these preliminary data do reveal a marked dependence of the ionic recombination coefficient on the pressure

of the third body. This has direct relevance to stratospheric de-ionization and has enabled us to make somewhat better estimates of the most appropriate recombination coefficients for these regions.

EXPERIMENTAL

The FALP technique has been discussed in detail previously (Smith et al., 1975; Adams et al., 1975; Smith and Church, 1976) and only the salient features will be mentioned here. Ionization is created by a microwave cavity discharge in the upstream region of a fast-flowing helium carrier gas and a thermalized electron - positive ion afterglow plasma is generated downstream of the discharge and distributed along the length of a flow tube. The addition of an appropriate amount of an electron attaching gas either upstream or downstream of the discharge results in the generation of characteristic negative ions and positive ions in the plasma and the total removal of electrons. At sufficiently high helium pressures (≥ 0.4 torr) and positive ion/negative ion number densities (n_+ , n_-), the ion-ion plasma becomes recombination controlled and ionic recombination coefficients can then be determined by measuring the ion density gradient down the flow tube and the plasma flow velocity (Adams et al 1975) using our Langmuir probe technique. The ionic species present in the after glow plasma are determined using a downstream quadrupole mass spectrometer/detection system and additionally the relative masses of the positive and negative ions (m_+/m_-) can be determined at any point in the plasma using the Langmuir probe which serves as a check on the downstream mass spectrometer mass identifications.

The two reactions chosen for study ((3) and (4)) have previously been studied in some detail at low pressures (< 1 Torr) where only pure binary mutual neutralization occurs (Smith and Church, 1976, 1977; Church and Smith, 1977) and the experimental details relating to the generation of the

particular ion-ion plasmas are given in the relevant references. It is sufficient to say that the reactant gases used for these reactions were NO_2 for (3) and SF_6 for (4). The maximum pressure at which we could study these reactions was about 8 Torr as a result of the loss of ionization density in the downstream measurement zone of the flow tube and inadequate ion current reaching the mass spectrometer preventing positive identification of the ions present in the plasma. This was a direct result of the necessity to throttle the Roots pump (used to flow the helium carrier gas) in order to raise the helium pressure which reduced the carrier gas flow velocity, the amount of ionization extracted from the discharge and the density of plasma flowing into the downstream measuring zone. In the study of recombination reactions of stratospheric significance it would obviously have been more appropriate to use a nitrogen carrier gas. However the microwave discharge in pure N_2 is extremely noisy and unfortunately prevented satisfactory operation of the Langmuir probe in the afterglow of this discharge.

The Langmuir probe technique is described in detail in the references already cited, but it is important here to refer to a potential problem when they are used at relatively high gas pressures. In our approach, positive and negative ion number densities are determined from an analysis of the current-voltage characteristics obtained in the so-called orbital-limited-current régime. In this analysis, it is required that no collisions occur between the ions and the ambient gas atoms or molecules within the space charge sheath which surrounds the positively or negatively biased probe. When this and other well-defined criteria (involving such parameters as the probe size and the plasma density etc.) are satisfied then a plot of probe current squared (i^2) against probe potential with respect to the plasma potential (V) should be linear and n_+ or n_- can be obtained directly from the slope of the line. Such is to be expected

under the conditions of our experiments at low helium pressures and indeed has been observed to be so in the numerous experiments we have carried out to determine binary ion-ion recombination coefficients (see cited references).

However, as the pressure is raised ion collisions must eventually occur within the space charge sheath and therefore, at the higher pressures of the present experiments, one has to be cognizant of potential problems involving such collisions. Such have been investigated both theoretically and experimentally by Schulz and Brown (1955) whose data show obvious and predictable departures from the linearity in the i^2 versus V plots when collisions occur in the space charge sheath. Thus we have used the linearity of the i^2 versus V plots in our experiments as indicators of the absence of significant sheath/collisions problems. Such problems would result in upcurving of the plots (not observed) and erroneously high ion densities. The latter would then result in an downcurving of the reciprocal density versus time plots from which the recombination coefficients are deduced. The reciprocal density plots obtained for the $\text{NO}^+ + \text{NO}_2^-$ reaction are given in Fig. 1. The linearity of these curves is taken as additional evidence for the validity of the probe technique. The considerable amount of work done in relation to the operation of Langmuir probes under various conditions of charged particle density, gas pressure etc. is summarized in the book by Swift and Schwar (1970).

RESULTS

The effective binary recombination coefficients, α'_2 , for reaction (3) were obtained from the slopes of the curves given in Fig. 1. Similar data were obtained for reaction (4) and the values of α'_2 obtained at the several pressures at 300K for both reactions are given

in Table 1 together with our previously published data for the pure binary coefficients, α_2 . These data are presented graphically in Fig. 2 where it is apparent that in both reactions α'_2 is sensibly independent of pressure below ~ 1 Torr i.e. $\alpha'_2 (< 1 \text{ Torr}) \approx \alpha_2$, the pure binary rate. Note the excellent agreement of α_2 with the previously published values, corroborating the previous result that α_2 for reaction (3) is significantly larger than that for reaction (4). However, above ~ 1 Torr, α'_2 for both reactions clearly increases with increasing pressure, the increase being significantly greater for reaction (4) than for reaction (3). Clearly within this low pressure range α'_2 does not vary linearly with pressure as predicted by the Thomson ternary mechanism which has been shown to be valid experimentally at high pressures (Bahan and Person, 1964, hereafter termed HP). Rather, the form of both the curves given in Fig. 2 can be described as an exponentially increasing α'_2 with helium pressure, viz:

$$\alpha'_2 = \alpha_2 \exp (Cp) \quad (5)$$

where α_2 is the low pressure limiting value, previously described as the pressure invariant, pure binary value. Thus for reactions (3) and (4) respectively we have that at 300K in the pressure range 0-8 Torr:

$$\alpha'_2 = 6(-8) \exp \left[\frac{-p}{5} \right] \text{ cm}^3 \text{ s}^{-1} \quad (6)$$

$$\alpha'_2 = 4(-8) \exp \left[\frac{-p}{5} \right] \text{ cm}^3 \text{ s}^{-1} \quad (7)$$

where the exponents have units of Torr⁻¹. The more rapid rise of α'_2 for reaction (4) relative to reaction (3) is now seen as a larger exponent in (7) than in (6), these being in the approximate ratio of 1.8: 1. Significantly, this is close to the inverse ratio of the mean free path of the heavier ions (SF_3^+ , SF_5^+) relative to the lighter ions (NO^+ , NO_2^+) in helium as calculated from the zero field mobilities in helium (McDaniel and Mason 1973, Smith and Church, 1976) using the Langevin expression (Loeb, 1955). The mean free paths are indicators

of the degree of collisional coupling between the accelerated ions and the helium atoms. A similar correlation has been observed by Mahan and Person (1964) between the mean free path of NO^+ , NO_2^- ions in various gases and the ternary recombination coefficients of these ions in the higher pressure (Thomson) régime.

Equation (5) can now perhaps be re-written as

$$\alpha'_2 = \alpha_2 \exp \left[-\frac{Cp}{\lambda} \right] \quad (3)$$

where λ is the mean free path of the ions in the helium. What then is the mechanism operating in this low pressure region which causes the variation α'_2 with pressure to differ from that in the Thomson régime? We can only offer a qualitative explanation to this in which we envisage that collisions of the ions occur with the helium atoms at large distances of separation of the positive and negative ions, R , before they have gained appreciable kinetic energy via acceleration in their mutual Coulombic field i.e. when $kT \gtrsim e^2/R$. Under these circumstances, the ions will effectively be "cooled" below the "temperature" they would otherwise possess in the absence of collisions and a corresponding increase in the mutual neutralization rate will occur (as is referred to in the Introduction). Thus we view the process as "collisionally-enhanced mutual neutralization" whereby the collisions at large separation distances do not result in trapping of the ions followed by inevitable neutralization (as envisaged in the Thomson mechanism) but rather the modification of the factors which influence the mutual neutralization rate (e.g. expansion of the "absorbing sphere". See the review by Moseley et al 1975). This is very like the process which Bates and Mendas (1970b) suggest and formulate for very low gas densities.

We also do not have a convincing explanation for the apparent exponential increase of α'_2 with pressure more than to suggest that it is reminiscent of the loss of energy of particles traversing a resistive

medium (an exponential fall in temperature of the ions in the very weak part of the Coulombic field?). Clearly, the exponential increase of α'_2 cannot be maintained up to pressures much greater than the maximum available in our experiment. The MP data for $\text{NO}^+ + \text{NO}_2^-$ in helium at higher pressures conforms with the Thomson mechanism ($(\alpha'_2 - \alpha_2) \sim P$) and so our lower pressure data must merge with these (to within any normalization errors) as we have indicated in Fig. 3. The MP data in helium indicated by the dashed line is a linear extrapolation of the MP data from pressures greater than 50 Torr and is subject to appreciable variation due to the large extrapolation. This figure also forcibly indicates, as recognised previously, the dangers in extrapolating higher pressure data in order to obtain binary recombination coefficients. It also refutes the concept of a pressure independent ternary ionic recombination coefficient (since α'_2 is not linearly dependent on pressure as is recognised implicitly in theoretical models (e.g. Bates and Kendra, 1975)) which we have been forced to use previously in atmospheric modelling (Smith and Church, 1977).

A final point to note before discussing the stratospheric implications of the present data is that any hidden complications due to operating the Langmuir probes at high pressures (sheath collisions etc. discussed in the Experimental section) would finally result in the anomalous reduction of α'_2 , so the increase in α'_2 with increasing pressure is indeed a real enhancement of the recombination coefficients.

STRATOSPHERIC IMPLICATIONS

A rapid rise in α'_2 in the very low pressure regime indicated by the present data could not have been accounted for in previous estimates of atmospheric de-ionization rates. The rate of increase of α'_2

depends on the nature of the interacting ions and we have suggested that an important parameter is the mean free path of the ions in the ambient gas (relation (8)). In the stratospheric the positive and negative ions are known to be large clustered species e.g. $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and $\text{NO}_3^-(\text{HNO}_3)_m$ (Arnold et al., 1977, 1978; Arnold and Fabian, 1980; Arijs et al., 1978, 1980, 1981) and of course the ambient gas is largely N_2 . Therefore we need to estimate α'_2 for this combination of ion types recombining in N_2 . The MP data indicates clearly that N_2 is much more effective in the promotion of ternary recombination than helium (see Fig 3) which is quite consistent with the idea that λ is a prime indicator of the catalytic effect of ambient gas in ternary recombination. The λ values are again calculated from the zero field mobilities using the Langmuir expression (Loeb, 1955). Ionic mobilities in N_2 for simple and clustered ions are typically some seven times smaller than in helium, do not vary greatly with ionic mass and have actually been measured for several clustered positive ions (Dotan et al., 1976). Using the Langmuir expression, λ for these ions in N_2 is seen to be about three times smaller than in He. Therefore we expect that α'_2 will increase with pressure even more rapidly for cluster ions in N_2 than for the $\text{SF}_5^+/\text{SF}_5^-$ ions in helium. We assume (see Fig. 4) that α'_2 for this system will merge with the IE data obtained for (ostensibly) $\text{NO}^+/\text{NO}_2^-$ in N_2 at higher pressures (it is highly probable that the ions present in the MP experiments at the higher pressures were indeed cluster ions unless the gases used were extremely pure). So we have constructed the low pressure α'_2 curve adopting a pressure invariant value for α'_2 of $6(-7) \times 10^{-3} \text{ s}^{-1}$ at 500K, which we have recently shown to be a typical value for stratospheric-like ions (Smith et al., 1981), and using a value of λ in equation (8) which is three times that derived for the $\text{NO}^+/\text{NO}_2^-$ reaction.

Also in Fig. 3 we have included the MP data in K_2 adjusted to stratospheric temperatures (US Standard Atmosphere, 1976), adopting a T^{-3} temperature dependence for the three body rate coefficient (a compromise between the $T^{-2.5}$ and T^{-3} theoretical values and the T^{-4} experimental value of Fisk et al., 1967), and merged it with our low pressure curve adjusted only as T^{-3} (assuming that in this region the process is largely "collisionally enhanced binary recombination" as discussed above). The rapid increase in α'_2 at low pressure is similar in form to the theoretical curves predicted by Bates and Mendas (1978b) for molecular positive and negative ions recombining in oxygen, when a finite value of α_p is used in the calculations. Also it is interesting to note that when they apply this theoretical model to the high oxygen pressure data of McGowan (1967), fair overall agreement is obtained with an α_p value of $5(-8) \text{ cm}^3 \text{ s}^{-1}$, this being in good agreement with our previous values of α_p for many simple and clustered ions obtained using the FAL technique (see e.g. Smith et al., 1978).

We have included an altitude scale in Fig. 3 so that our best estimate of α'_2 at any point in the stratosphere can readily be obtained. The curve indicates that α'_2 rises rapidly below an altitude of about 45km at which $\alpha'_2 \approx \alpha_p$, i.e. pure binary ionic recombination, until about 40kms, $\alpha'_2 \approx 2\alpha_2$ i.e. the effective ionic recombination coefficient is approximately twice the typical pure binary coefficient. At an altitude of about 35kms at which several recent balloon-borne observations of stratospheric ions have been carried out (Arnold et al., 1977, 1978; Arnold and Fabian, 1980; Arijis et al., 1978, 1980, 1981), α'_2 has reached $\sim 2(-7) \text{ cm}^3 \text{ s}^{-1}$. At lower altitudes, α'_2 increases less rapidly with pressure as described by the higher pressure MP data adjusted to account for the

temperature gradients in the lower atmosphere.

CONCLUSIONS

The present data for two positive ion/negative ion neutralization reactions indicates a rapid increase in the neutralization coefficient, α'_2 , from the low pressure limiting value α_2 , for only a few Torr increase in the helium buffer gas pressure. Taking account of the relative efficiencies of nitrogen and helium as buffer gases, we conclude on the basis of a simple model and intuitive reasoning, which is given some credence by the higher pressure data of Mahan and Person (1964), that a rapid increase in α'_2 will occur in the stratosphere below about 45km altitude. An estimated five fold increase in α'_2 between 45 and 50km is indicated (see Fig. 3), a factor of about 2 greater than our previous estimates which were based only on the previous higher pressure data (Smith and Church, 1977). Our previously published data for the pure binary mutual neutralization reactions which occur in the mesosphere are confirmed by the present low pressure (<1 Torr) data.

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REFERENCES

- Adams, H.G., Church, H.J. and Smith, D. (1975) J. Phys. D: Appl. Phys. 8, 1409.
- Arijs, E., Ingels, J. and Nevejans, D. (1978). Nature, 271, 642.
- Arijs, E., Nevejans, D. and Ingels, J. (1980). Nature, 280, 634.
- Arijs, E., Nevejans, D., Frederick, P. and Ingels, J. (1981). Geophys. Res. Letts. (In Press).
- Arnold, F., Böhringer, H. and Henschen, G. (1976). Geophys. Res. Letts. 3, 653.
- Arnold, F., Frankowsky, D. and Marion, E.H. (1977). Nature. 267, 30.
- Arnold, F. (1980) Proceedings of the ESA Symposium on Rocket and Balloon Programmes. Bournemouth, England.
- Arnold, F. and Fabian, R. (1980). Nature. 283, 45.
- Bates, D.R. (1979). Adv. Atom. Molec. Phys. 15, 235.
- Bates, D.R. and Moffett, R.J. (1966). Proc. Roy. Soc. (Lond.). A301, 1.
- Bates, D.R. and Flannery M.R. (1967). Proc. Roy. Soc. (Lond.). A301, 547.
- Bates, D.R. and Mendon, I. (1975). J. Phys. B: Atom. Molec. Phys. 8, 1770.
- Bates, D.R. and Mendon, I. (1976a). Proc. Roy. Soc. (Lond.). A359, 275.
- Bates, D.R. and Mendon, I. (1976b), Proc. Roy. Soc. (Lond.). A359, 287.
- Church, H.J. and Smith, D. (1977). Int. J. Mass Spectrom. Ion. Phys. 23, 137.
- Dotan, I., Albritton, D.L., Lindinger, W. and Pahl, M. (1976). J. Chem. Phys. 65, 5078.

Fisk, G.A., Mahan, B.H. and Lark, E.K. (1967). J. Chem. Phys. 47, 2649

Flannery, M.R. (1974). "Case Studies in Atomic Collision Physics" (Eds E.W. McDaniel and M.R.C. McDowell) Vol. 2, p.1. North Holland Publ. Co., Amsterdam.

Flannery, M.R. (1976). "Atomic Processes and Applications". (Eds. P.G. Burke and B.L. Moiseiwitsch) p. 409 North Holland. Publ. Co. Amsterdam.

Loeb, L.B. (1954) "Basic Processes of Gaseous Electronics" p.42. Univ. of California Press, Berkeley.

Mahan, B.H. (1971). "Advances in Chemical Physics" (Eds I. Prigogine and S.A. Rice) Vol. 23 p.1. Wiley, New York.

Mahan, B.H. and Lark, E.K. (1964). J. Chem. Phys. 40, 391.

McGowan, E. (1967). Can. J. Phys. 45, 439.

Moreley, J.L., Olson, E.E. and Peterson, J.K. (1975). "Case Studies in Atomic Physics", Vol. 5. p.1. North Holland Publ. Co., Amsterdam.

McDaniel, E.W. and Mason, E.A. (1977). "The Mobility and Diffusion of Ions in Gases" p.266. Wiley, New York.

Olson, E.E. (1977). J. Chem. Phys. 56, 2979.

Pyper, J. (1967). "Atomic and Molecular Processes". (Ed. D.R. Bates) p. 211. Academic Press, New York.

Schultz, G.J. and Brown, R.G. (1966). Phys. Rev. 151, 1647.

Sennhauser, H.S. and Armstrong, D.A. (1978a). Radiat. Phys. Chem. 11, 17.

Sennhauser, H.S. and Armstrong, D.A. (1978b). Radiat. Phys. Chem. 12, 111.

Smith, D., Adams, N.G., Dean, A.G. and Church, M.J. (1975). J. Phys.

D: Appl. Phys. 8, 141.

Smith, D., Adams, N.G. and Church, M.J. (1976). Planet. Space Sci. 24, 697.

Smith, D. and Church, M.J. (1976). Int. J. Mass Spectrom. Ion Phys. 19, 115.

Smith, D. and Church, M.J. (1977). Planet. Space Sci. 25, 437.

Smith, D., Church, M.J. and Miller, T.M. (1978). J. Chem. Phys. 68, 1794.

Smith, D. and Adams, N.G. (1980). "Topics in Current Chemistry" (Eds. H. Venugopalan and S. Vepřek). Vol. 89. p.1. Springer Verlag, Berlin.

Smith, D., Adams, N.G. and Alge, E. (1981). Planet. Space Sci. (In Press).

Swift, J.D. and Schwar, M.J. (1970). "Electrical Probes for Plasma Diagnostics". p. 184. Iliffe, London.

U.S. Standard Atmosphere. (1976). National Aeronautics and Space Administration, United States Air Force, Washington D.C.

FIGURES AND TABLE CAPTIONS

Fig. 1 Plots of reciprocal positive ion density, n_+^{-1} , versus afterglow time in $\text{NO}^+/\text{NO}_2^-$ afterglow plasmas at the several pressures (in Torr) indicated at 300K. Values of α'_2 for the $\text{NO}^+ + \text{NO}_2^-$ reaction are obtained from the best fit lines through the points and are given in Table 1 and Fig. 2.

Fig. 2 Value of α'_2 as a function of helium pressure at 300K for the two reactions indicated. Also indicated are the values previously obtained at low pressures by the authors indicated (see also Table 1). The solid curves are described by the exponential relations for α'_2 given in the text.

Fig. 3 The data for α'_2 from Table 1 plotted on a compressed pressure scale so as to include the higher pressure MP data ostensibly relevant to the reactions of $\text{NO}^+ + \text{NO}_2^-$ in both helium and nitrogen. Values of α'_2 as a function of altitude in the stratosphere (top scale) are also given as estimated from the higher pressure MP data in N_2 and from the simple model derived from the present low pressure data (see text).

Table 1. Values of α'_2 as a function of helium pressure for the two reactions indicated. Also given are the previous values of α_2 obtained in helium.

TABLE 1

Reaction	He Pressure (Torr)	$\alpha_2' \times 10^8$ (cm ³ s ⁻¹)
NO ⁺ + NO ₂ ⁻	0.5	6.3 *
	0.7	6.4 *
	0.54	6.7
	1.1	7.3
	2.2	7.9
	4.2	9.6
	7.6	14.7
SF ₃ ⁺ + SF ₅ ⁻	0.7	4.0 /
	0.6	4.1
	2.1	4.8
	4.1	7.5
	8.1	19.4

* Smith and Church, 1976.

/ Church and Smith, 1977.

FIG. 1

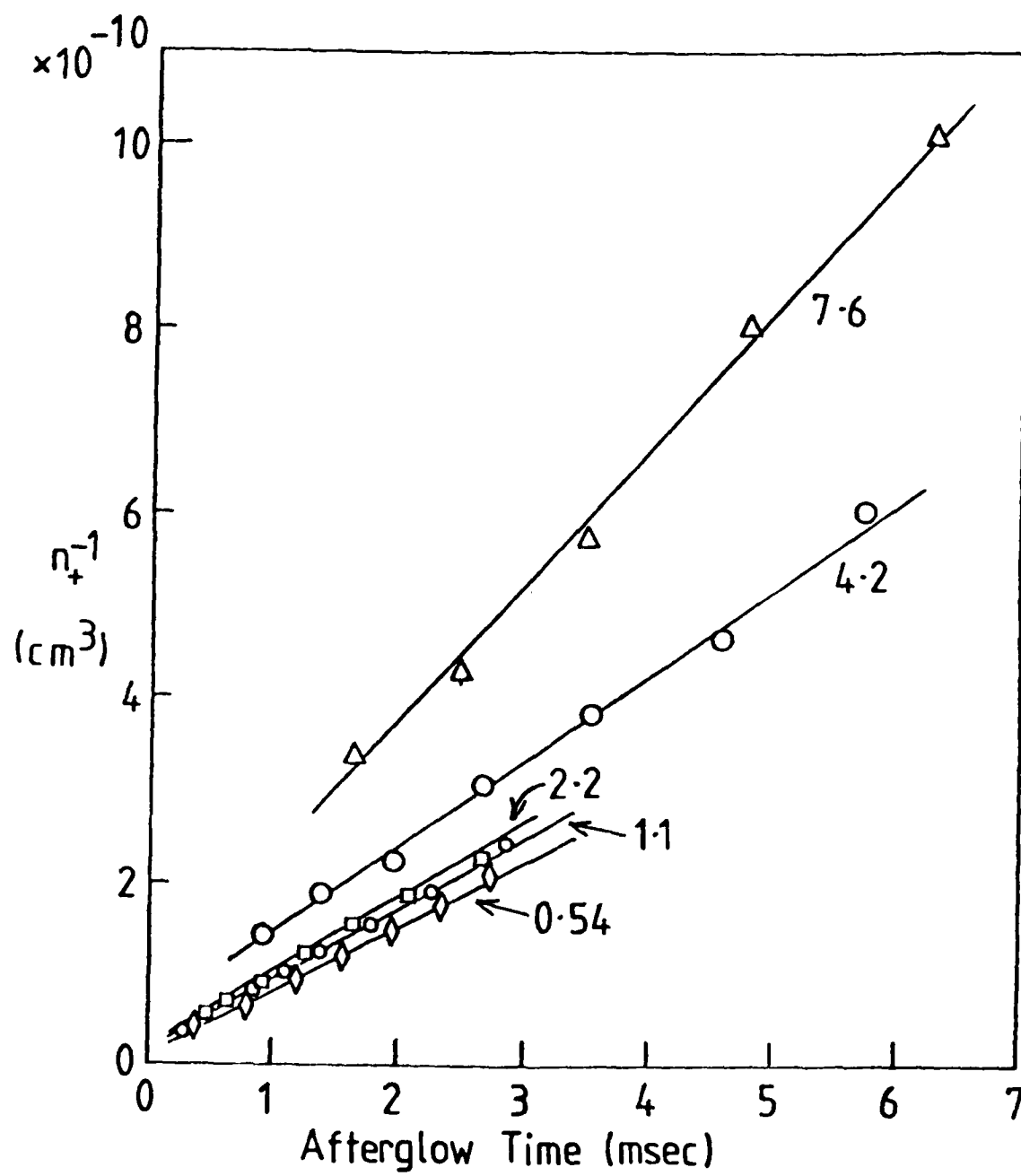


FIG. 2

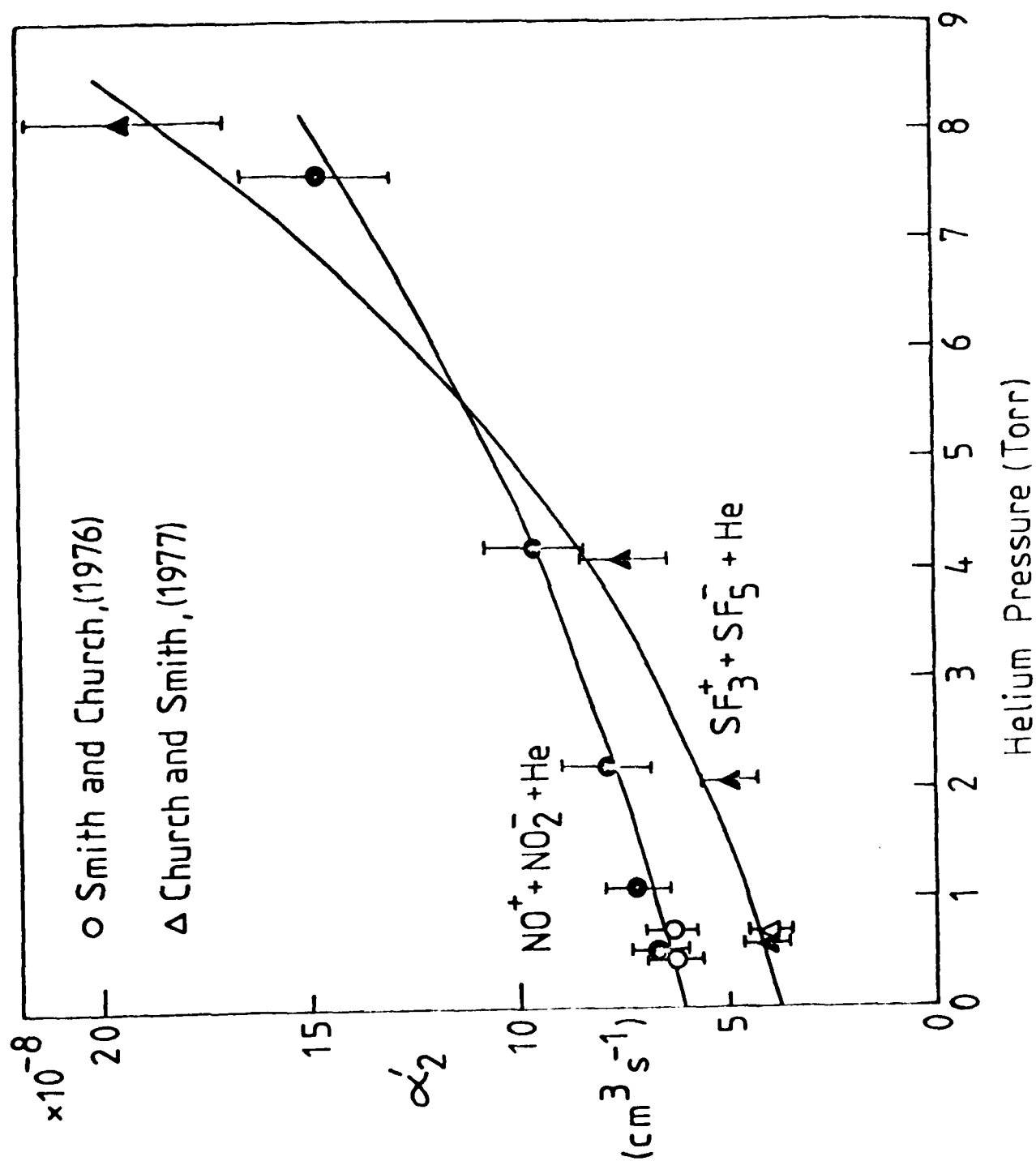
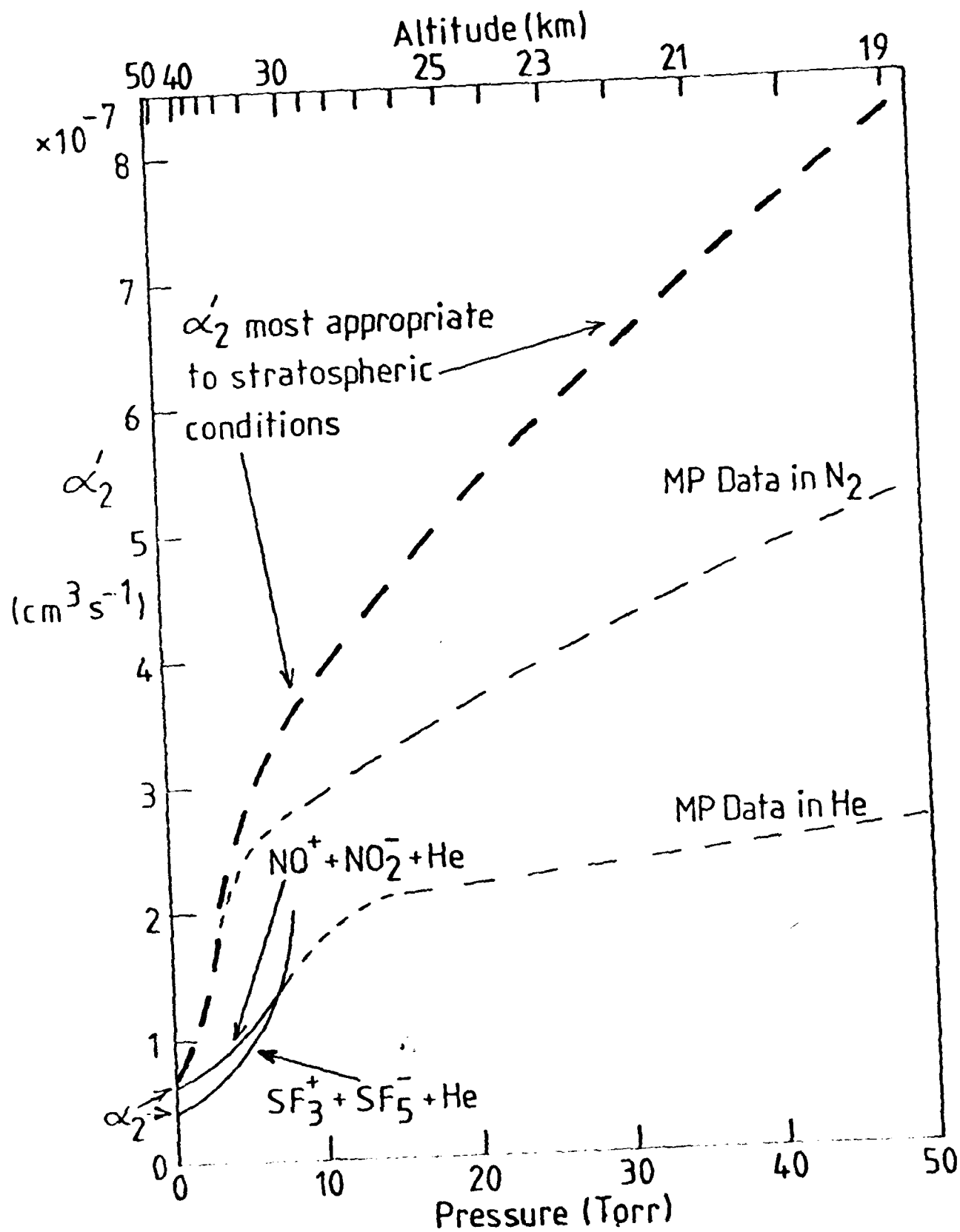


FIG. 5



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